

Chapter 2

Stress-Relaxation Behavior of Poly(Methyl Methacrylate) (PMMA) Across the Glass Transition Temperature

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Abstract Characterizing Poly(methyl methacrylate) (PMMA) across its glass transition temperature is essential for modeling warm deformation processes such as hot embossing. Its mechanical properties vary significantly across the glass transition as well as with strain rate. Several previous models have attempted to capture this behavior utilizing uniaxial compression experimental data with limited success. In this work, compression experiments including stress relaxation at large strains are conducted to aid researchers in developing better models. Multiple temperatures, final strains, and strain rates are examined to characterize the material across values found in typical hot-embossing processes. It was found that the amount of stress relaxed is highly dependent on the temperature and strain at which it is held. With this data, a model can be developed that will accurately capture stress relaxation with the final goal of being able to simulate hot embossing processes.

Keywords PMMA • Glass transition • Stress relaxation

2.1 Introduction

Hot embossing or nanoimprint lithography is a process that is used to impose micro- and nano- scale surface features on a polymer. Applications of hot embossing include the molding of microchannels or optical arrays [1]. The polymer is heated past its glass transition temperature, T_g , and a finite deformation is applied to the stamp. For a period of time, this position is held at the original elevated temperature, allowing the polymer to flow and fill in the stamp. Next, it is cooled and unmolded simultaneously as shown in Fig. 2.1. The inherent sensitivity of the polymer's mechanical behavior near the glass transition combined with the many process variables involved make predicting the process outcome challenging. Polymers are known to be highly sensitive to both temperature change and strain rate near the glass transition. In addition, the final strain and hold time during the process significantly affect the outcome [2]. As a result, it is difficult and expensive to develop an optimized process through experiments alone and a predictive material model has the potential to greatly improve the process. Hot embossing is already embraced as a low-cost environmentally friendly fabrication technique and the ability to optimize the process will only increase its attractiveness.

At the conditions at which hot embossing is performed, polymers are highly sensitive to strain rate and variation of temperature [2]. One polymer commonly used in hot embossing is Poly(methyl methacrylate) (PMMA). PMMA is an amorphous thermoplastic with a glass transition temperature of approximately 105–110 °C that makes it ideal for the process of hot embossing [3]. While previous experiments have shown that its capability in hot embossing [1, 3], optimization of the fabrication technique is challenging to develop a large-scale production of these devices. Several models have been developed to try and capture the behavior of PMMA around glass transition temperature [4–8]. The majority of the models developed have been based on uniaxial compression experiments [4–7]. While the models are largely able to capture the behavior in uniaxial compression, they are still unable to predict the correct amount of spring-back present in hot embossing. It is believed that they fail to capture the behavior because none adequately capture stress relaxation of the polymer.

Stress relaxation is present in the process of hot embossing during the hold period after the deformation is applied. To accurately design a model, experimental stress relaxation data of PMMA in compression at small and large strains is needed.

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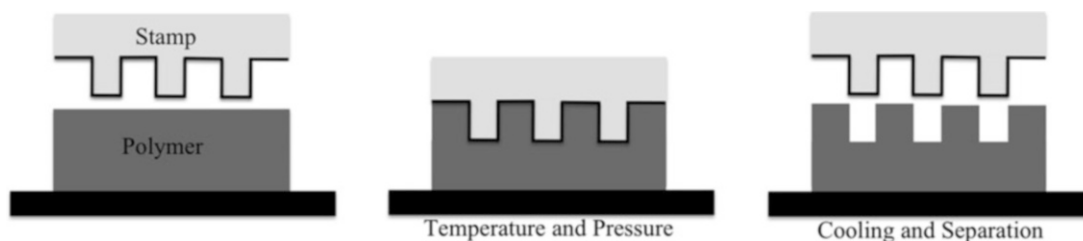


Fig. 2.1 (a) The polymer and stamp are heated to a temperature above glass transition (b) The stamp is lowered and pressure is applied to the polymer forcing the polymer to flow and fill in the voids (c) The polymer and stamp are cooled briefly while still in contact then separated with cooling continuing

The majority of stress relaxation data available on PMMA is based on the works of McLoughlin and Tobolsky that found a master relaxation curve for PMMA at small tensile strains [9]. Others have also performed stress relaxation experiments on PMMA at small tensile strains [8], multiaxial compression [10], and torsion [11] but little to no data is found at large compressive strains during relaxation. It is important to study the relaxation behavior of PMMA at large compressive strains because in hot embossing, large local compressive strains will occur that need to be accurately captured during a finite element simulation. The purpose of these experiments is to provide necessary data to quantify the amount of stress relaxation present in PMMA at temperatures, strain rates, and final strains found in hot embossing to better predict the spring-back.

2.2 Experimental

PMMA cylinders were cut from commercial sheet stock supplied by Plaskolite, Inc. to an initial height and diameter of 8.8 and 10 mm respectively. An Instron 5869 screw driven materials testing system was used in conjunction with an Instron 3119–409 environmental chamber to heat the samples to the specified temperature. An Instron 5800 controller running Instron Bluehill software controlled the load frame. Displacement of the upper compression plate was controlled and the force recorded with a 50 kN load cell. Using the displacement and force data, true stress and true strain were calculated, using the initial dimensions of the sample and the assumption that volume remained constant. Samples were tested using a ramp-hold loading history, where the ramp was a constant true strain rate followed by a hold at a specific final strain. Two loading strain rates ($-1.0/\text{min}$ and $-3.0/\text{min}$), three final true strains (-0.5 , -1.0 , -1.5) and five temperatures (95 – 135 °C) composed the testing matrix. All samples were placed in a dessicant chamber at least 24 h prior to the test to control the amount of moisture present. Teflon sheets were placed between the compression plates and sample to reduce friction. WD-40 was applied between the compression plates and Teflon film to provide additional lubrication. Each sample was placed in the pre-heated environmental chamber for 30 min prior to testing to ensure the entire sample was at the testing temperature. To ensure repeatability, each test was run twice.

2.3 Results

At temperatures less than T_g PMMA behaves as a viscoelastic solid. There is an initial region of elastic behavior followed by a small period of strain softening as evident in Fig. 2.2. The strain softening is attributed to aging of the polymer, which decreases the free volume of the polymer and thereby causes an elevated yield stress at small strains. If the polymer were heated past T_g and quenched the free volume would increase and the strain softening would no longer be present [12]. As the temperature is increased the strain softening effects diminish and are no longer present at temperatures greater than T_g as shown in Fig. 2.3. Another temperature dependent region is the elastic portion at small strains. When the temperature is greater than transition, the elastic region essentially disappears and the polymer behaves more fluid-like. After the initial yield, the material begins to exhibit strain hardening attributed primarily to molecular orientation. At higher temperatures, the amount of strain hardening decreases as shown in Fig. 2.4.

During the hold period, stress relaxation occurs and is highly dependent on temperature and the strain at which it is held. At temperatures less than T_g there is a large initial drop in the stress. After this initial drop, the polymer continues to relax, although the rate of relaxation remains at a lower, more constant rate. At temperatures near the glass transition, there is still a small region of an initial drop once the hold period begins, however it is less severe than at lower temperatures. Similar to the

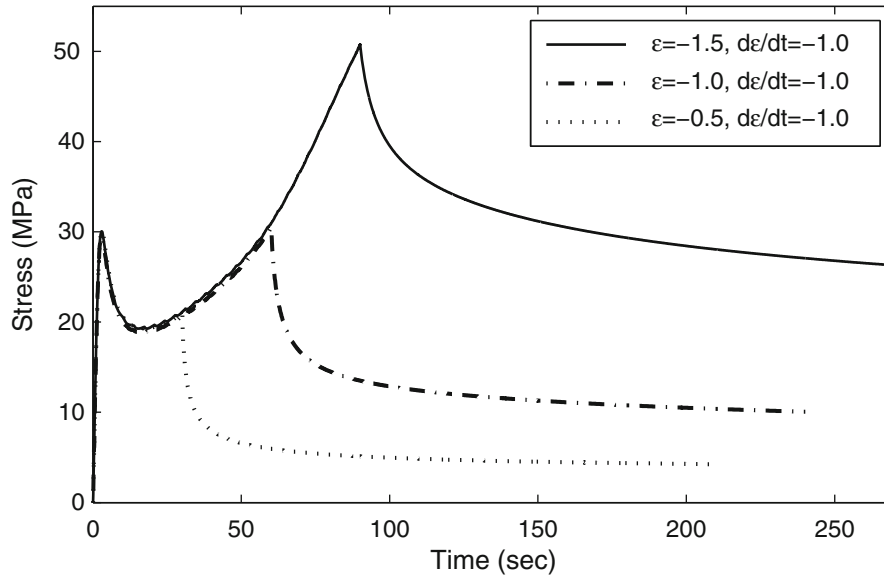


Fig. 2.2 Stress versus time at 95 °C for samples loaded at a rate of $-1.0/\text{min}$ and held for 180 s. Each sample was held at a different final strain: -0.5 , -1.0 , and -1.5

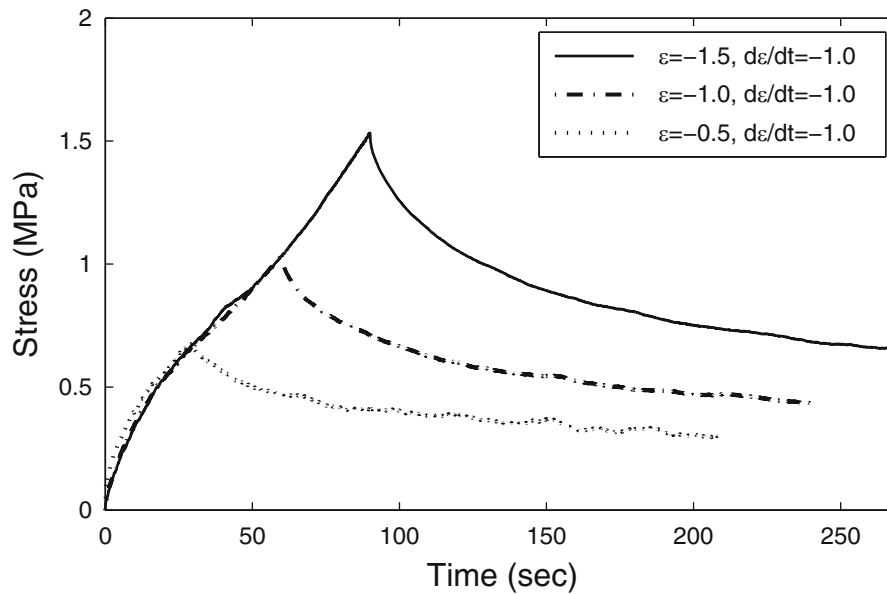


Fig. 2.3 Stress versus time at 135 °C for samples loaded at a rate of $-1.0/\text{min}$ and held for 180 s. Each sample was held at a different final strain: -0.5 , -1.0 , and -1.5

low temperatures, it reaches a smaller, more constant relaxation rate after this initial drop. Much less of an initial drop is present in the stress at the beginning of the hold period at temperatures greater than transition. For a given held strain and temperature, strain rate does not affect the final relaxation value. As shown in Figs. 2.5, 2.6 and 2.7 the higher strain rate values cause a larger initial drop in the stress than a lower strain rate at the same held strain. However, the steady stress it relaxes to is approximately the same as its lower strain rate counterpart.

To quantify the amount of stress-relaxation, the percent relaxed is calculated to give an idea of relative relaxation amounts. The percent relaxed is calculated for each temperature and held strain by subtracting the steady relaxation stress from the maximum stress achieved before the hold period and dividing by the maximum stress. At temperatures less than

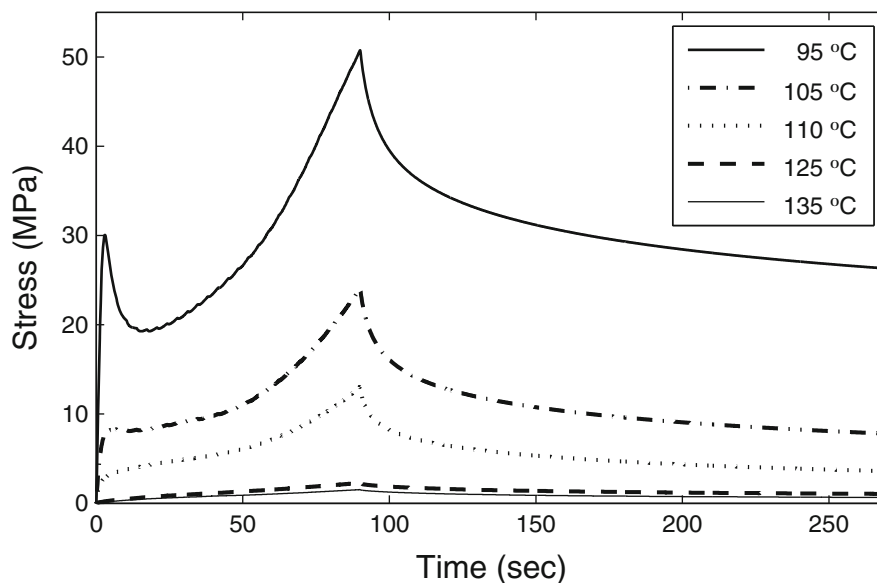


Fig. 2.4 Stress versus time for samples loaded at a rate of $-1.0/\text{min}$ and held at a strain of -1.5 . Each sample was at a different temperature: $95\text{ }^{\circ}\text{C}$, $105\text{ }^{\circ}\text{C}$, $110\text{ }^{\circ}\text{C}$, $125\text{ }^{\circ}\text{C}$, or $135\text{ }^{\circ}\text{C}$

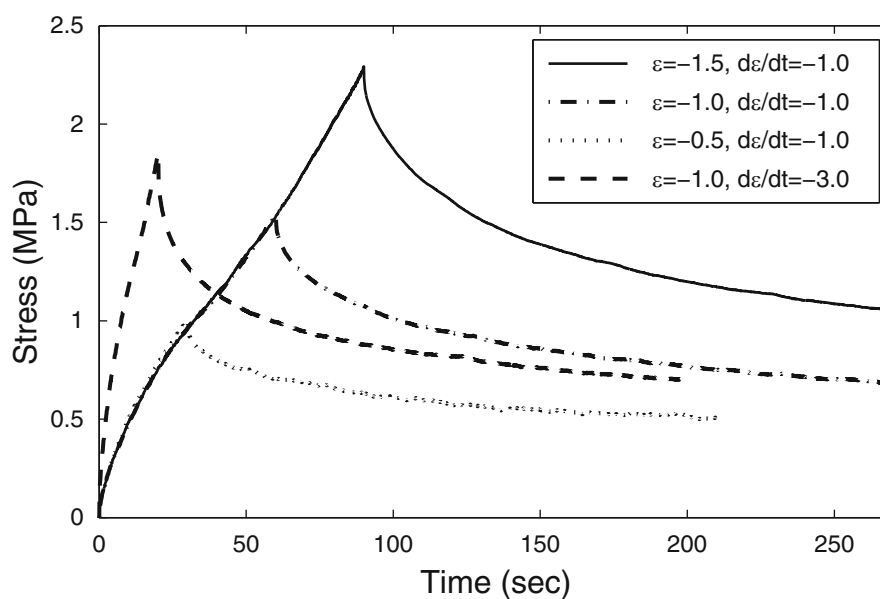


Fig. 2.5 Stress versus time at $125\text{ }^{\circ}\text{C}$ for samples loaded at a rate of either $-1.0/\text{min}$ or $-3.0/\text{min}$ and held for 180 s. Each sample was held a different final strain: -0.5 , -1.0 , or -1.5

glass transition, holding at a small strain will cause more stress-relaxation than if it were held at a larger strain. This is true only for temperatures less than transition as evident in Fig. 2.8. At temperatures around glass transition, $105\text{--}110\text{ }^{\circ}\text{C}$, the trend begins to decrease and the percent relaxed at different final strains becomes about the same. At temperatures greater than glass transition, $125\text{ }^{\circ}\text{C}$ and $135\text{ }^{\circ}\text{C}$, smaller hold strains cause less stress relaxation than at large strains, opposite of what was found at low temperatures.

The relaxation effects can be explained by looking at how polymer molecules move depending on temperature and strain. At temperatures less than T_g the polymer molecules do not flow readily and take larger amounts of time to rearrange

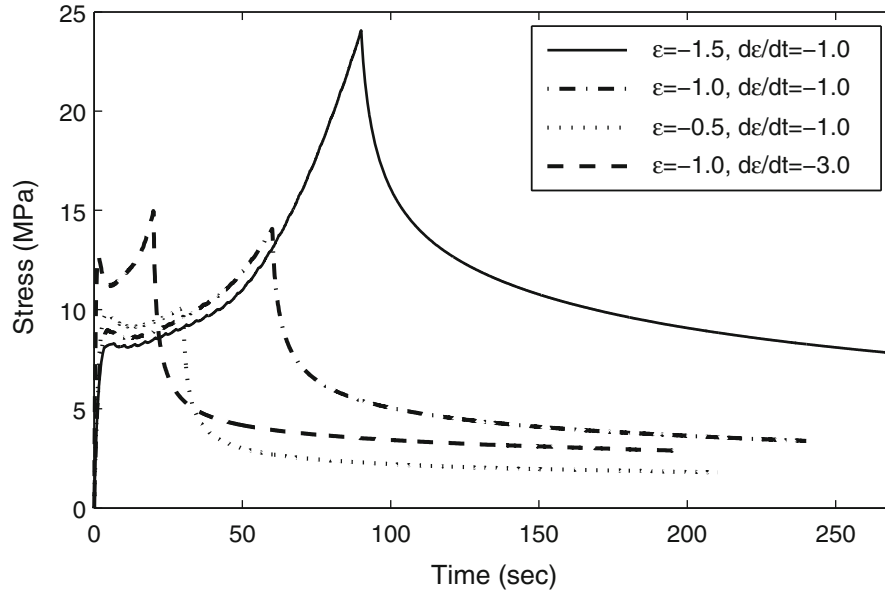


Fig. 2.6 Stress versus time at 105 °C for samples loaded at a rate of either $-1.0/\text{min}$ or $-3.0/\text{min}$ and held for 180 s. Each sample was held a different final strain: -0.5 , -1.0 , or -1.5

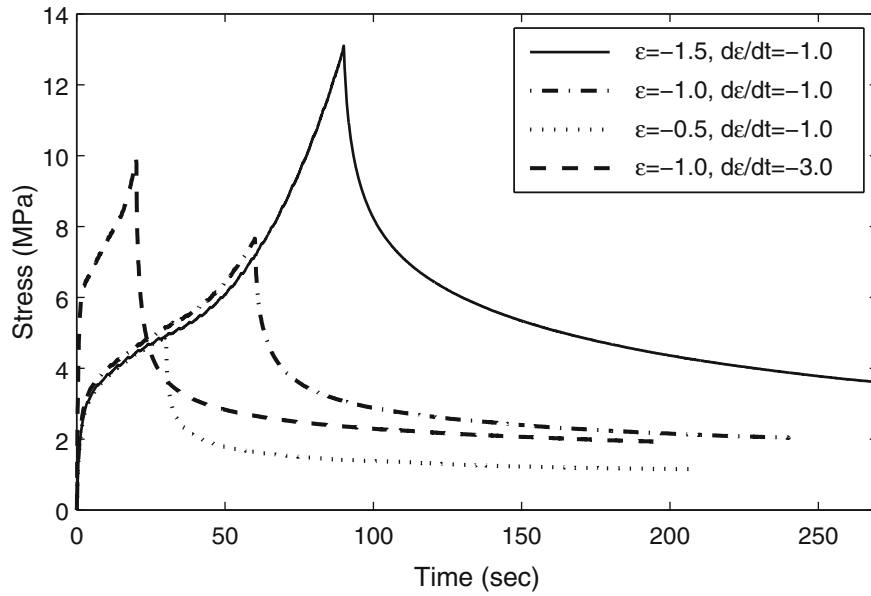


Fig. 2.7 Stress versus time at 110 °C for samples loaded at a rate of either $-1.0/\text{min}$ or $-3.0/\text{min}$ and held for 180 s. Each sample was held a different final strain: -0.5 , -1.0 , or -1.5

themselves to reduce the stress. At small strains, the polymer molecules have not begun to align, like they do at large strains. This lack of alignment allows them to rearrange to obtain a low stress state during the hold period. The highly oriented molecules at large strains do not rearrange easily, which causes them to reach a higher steady stress state. At temperatures greater than T_g the molecules flow readily and are immediately able to arrange themselves into as low of a stress state as possible, even during loading. Therefore, at low strains they have already arranged themselves with the lowest stress-state so there is little stress to relax. While at large strains, more imperfections in the arrangement have accumulated that can be relaxed during the hold period. This effect also explains the large amount of relaxation that occurs with high strain rates.

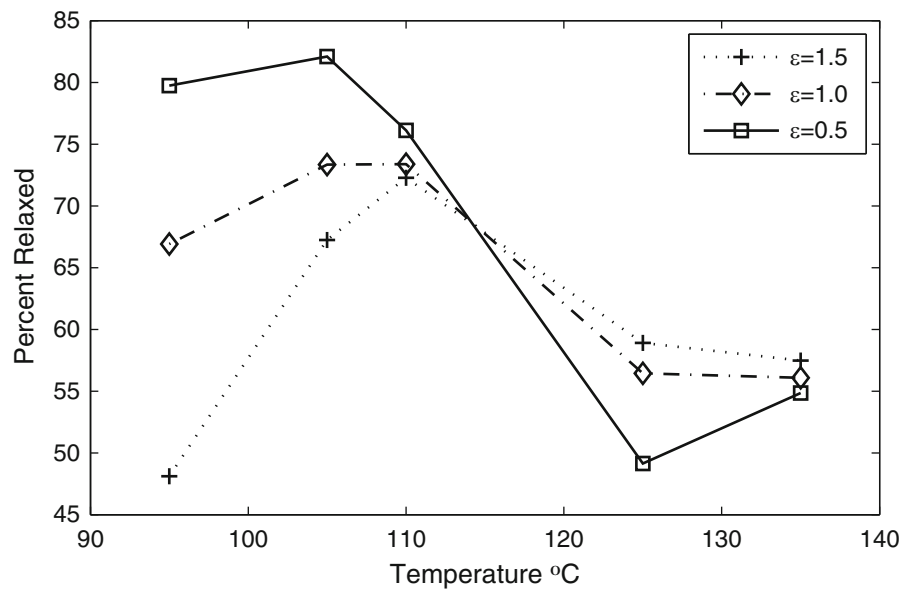


Fig. 2.8 Percent of stress relaxed versus temperature for samples loaded at a rate of $-1.0/\text{min}$ and held at -1.5 , -1.0 or -0.5 final strain. The percent relaxed is the difference between the maximum stress and the steady relaxation stress, divided by the maximum stress for a given temperature and held strain

When looking at Figs. 2.5, 2.6 and 2.7, when a faster strain rate is used, a larger amount of stress is generated prior to the hold period compared to its low strain rate counterpart. This is because the polymer is not allowed the time necessary for it to arrange into its lowest stress state. Once it is allowed to relax, it approaches the same steady relaxation stress as that of the low strain rate sample.

2.4 Conclusions

With this new data, a new constitutive model can be developed to capture the behavior present. This model will need to capture the stress relaxation behavior at multiple strains, strain rates, and temperatures in order for it to successfully predict hot embossing processes. Additional data examining how PMMA behaves during cooling and actual hot embossing processes need to be obtained so the material model can be validated for use in a finite element program. However, with this new data, a material model can be developed that will predict stress relaxation behavior of PMMA.

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